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In re Application of:  
Michaud, Sroka, and Winkelmann

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SURFACE FINISHING

Group Art Unit: 3723

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**DECLARATION OF GARY SROKA**

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I Gary J. Sroka, Ph. D., of Missouri City, TX, hereby declare as follows:

1. I am the Research and Development Manager for REM Chemicals, Inc. in Brenham, TX, and am a co-inventor of the above referenced invention. I have been working in the field of materials finishing for 7.5 years.
2. I received a Bachelor of Science in Chemistry from the University of Toronto in Ontario, Canada, and went to receive my Doctorate in Physical Chemistry from the University of Houston in Houston, Texas.
3. I have reviewed the Office Action dated December 19, 2003, and the rejections to the claims cited therein. I have also reviewed U.S. Patent No. 4,181,540, to Ahlf (hereinafter "Ahlf").

4. In attempting to repeat the Ahlf invention, a number of key elements are missing that would allow me to duplicate what Ahlf claims to have invented. Ahlf talks in generic terms of how to perform its invention, however, one of ordinary skill in the art needs very detailed information in order to finish the surface of a metal article. For instance, critical data that is missing from Example 1 of Ahlf, which includes the composition or the source of the manganese-iron phosphate complex used; the pH (acidity) of the manganese-iron phosphate complex; the concentration of the active ingredients of the manganese-iron phosphate complex; the identity of the type of cast iron used; and the hardness of the cast iron used. Furthermore, there is no disclosure in Ahlf that defines what is meant by a "highly polished" casting. No quantitative measurement of the surface roughness or useful qualitative information is provided so that one of skill in the art can be certain of when the "highly polished" casting is achieved. This information certainly must be provided to one having skill in the art in order to duplicate Example I without undue experimentation.
5. A world renowned phosphate expert wrote that it requires 30 seconds to coat iron with a single layer of manganese phosphate at an elevated temperature of 95 °C. Since the polishing mechanism of Ahlf is dependent on the rate of this reaction and since the rate of the reaction increases dramatically with temperature, it is impossible to obtain a polished surface in 10 seconds at ambient temperature as disclosed in Ahlf. Even if it were conceded that the phosphating step of Ahlf was 100 times faster than that reported in the literature, it still would require 1.85 hours to complete the polishing well in excess of the

10 seconds reported in Ahlf. Therefore, the polishing observed by the Ahlf was either a result of dissolution of the cast iron or the filling in of recesses by manganese phosphate or mechanical abrasion or a combination of these, none of which is the mechanism described and claimed in Ahlf.

6. Example 2 is also missing critical information necessary for one of skill in the art to repeat the Ahlf invention. Example 2 does not describe the aluminum alloy used, the rotational speed or pressure between the two mating aluminum surfaces, nor does it provide a quantitative or qualitative measurement of the "smooth, oxide coated surface". Again this information certainly must be provided to one having skill in the art in order to duplicate Example 2.
7. My attempts to duplicate the experiment in Example 2 also failed. Even while using very light hand pressure with a very slow relative motion of the mating surfaces, the aluminum was polished by mechanical abrasion rather than the mechanism described in Ahlf. Aluminum particles were formed by this abrading process and were clearly visible at 10X magnification. When the invention was tested using water instead of the dichromate solution, the aluminum surface was again polished with the formation of similar aluminum particles.
8. Therefore, the polishing mechanism was a result of mechanical abrasion and not the mechanism described in Ahlf. Even the inventor expressed uncertainty of the stock removal process when he stated "It is believed that aluminum oxide formed between the surface irregularities and was not abraded by the rubbing motion, but that aluminum

oxide which formed on high spots was broken away by abrasion, exposing bare aluminum to the dichromate solution for further oxidation.” (Column 4, line 14-18). Had he repeated this experiment using water instead of the dichromate solution he would have observed the same smoothing effect, and would have immediately known that the mechanism was merely abrasion and not the mechanism “believed” to be what was described in Ahlf.

9. I attempted to duplicate Example 1, and therefore read Example 1 thoroughly in light of the entire Ahlf specification.
10. Example 1 neither specifies the chemical composition of the manganese-iron phosphate complex nor identifies the commercial supplier. Obviously this information is critical to validating the invention. See Appendix 1, page 101 of The Chemical Surface Treatment of Metals (Ahlf prior art), which states: “In general terms, the growth of the coating is influenced by the concentration of metal ions and of phosphate ions in solution. The ratio of free to total phosphoric acid is of particular importance in this respect. Mixtures which are of practical use have mainly been protected by patents.”
11. Ahlf does not state whether or not oxidizing agents are present in the manganese phosphating solution. See Appendix 2, page 90 of The Chemical Surface Treatment of Metals (Ahlf prior art), which states that “The acid phosphating solutions which contain oxidizing agents behave very differently.” Since this information is vital, I was forced to make a major assumption as to which manganese-iron phosphate complex to use. NALCO, a renowned specialty chemical supplier, recommended with certainty that

NALCO AEROCOTE #4, a manganese phosphating solution for iron, is a suitable product to use.

12. No information is provided in Ahlf on the pH of the solution. Manganese phosphating uses chemicals having an acidic pH. This is again a very critical piece of information since the lower the pH of the manganese-iron phosphate complex the more likely dissolution is favored in the early stage of the phosphating mechanism over the mechanism described in Ahlf. See Appendix 1, page 101 of The Chemical Surface Treatment of Metals (Ahlf prior art), which comments that "If too much free phosphoric acid is present, the iron will be attacked too vigorously and the time to precipitation of the salts required for the coating process becomes longer. As a result the coatings are thin and have less protective value."
13. No information was supplied by Ahlf as to the concentration of the active products in the phosphating solution. This is a critical piece of information, as evidenced by prior art cited against Ahlf. See Appendix 1, page 101 of The Chemical Surface Treatment of Metals ('540 prior art), which states that: "If the heavy metal ion concentration is too low, the coating process is unsatisfactory even in solutions which contain oxidizing agents. Decrease in concentration of the phosphating medium itself also generally reduces the protective value of the coating." This forced me to make an assumption to use the AEROCOTE #4 at 100% concentration since the invention is carried out at ambient temperature and the Ahlf smoothing process occurs in only 10 seconds.

14. No specific information is provided in Ahlf on the composition of the cast iron or its hardness. Cast iron is a generic term for a high carbon, high silicon, iron alloy. There are five major types of cast iron: gray (most common), white, malleable, ductile, and special alloy). See Table 5-31 of Appendix 3. Again a critical piece of information is missing from Ahlf since different compositions of cast iron will have different reaction properties with manganese phosphating solutions. See Appendix 4, page 95 of The Chemical Surface Treatment of Metals (Ahlf prior art) which states that "Some data are available about the influence of increasing carbon content in steel on phosphating in manganese phosphate baths. In investigating normalised steels with carbon contents of 0.12, 0.29, 0.62 and 0.73 per cent, it was observed that, with increasing pearlite content, the crystal size of the phosphate coating increased. This has been ascribed to the fact that comparatively few nuclei are formed on the islets of pearlite." In the same paragraph as the above quote, it states that from testing done using zinc phosphating "it can be concluded that the carbon content will not exert any significant influence on the growth of the phosphate coatings from accelerated solutions which contain oxidizing agents." Ahlf does not give the formulation so that it is unknown whether or not an oxidizing agent was used in the manganese phosphate solution used in the invention. Since Ahlf mentions the presence of graphite flakes in the cast iron, I have to make a critical assumption that Ahlf used gray iron. See Appendix 4, page 81.
15. The hardness of the cast iron material is also not given in Ahlf. Again this is a critical piece of information since one having skill in the art understands that softer materials are

easier to machine, grind or polish than harder materials. Gray cast irons can have a wide range of hardnesses. See Appendix 4, Figure 5-34. It is important then to remember for the discussions that follow that cast irons are often “butter soft” relative to the hardened steel alloys used in my invention. Whereas gears and bearings are often hardened at their surface to a Rockwell Hardness Number C Scale of 60 HRC and greater, cast iron with a hardness of 110 -150 BHN has a hardness of much less than 1.0 HRC. See Appendix 5 for a comparison of the HRC versus the BHN hardness scales.

16. Furthermore, Ahlf does not provide a quantitative measurement of the “highly polished” surface. This again is critical information for one attempting to duplicate Example 1. The term “highly polished” is completely subjective and gives no quantitative measurement of the topography of the surface even though standards and equipment that can characterize surface properties were readily available and routinely used by one having skill in the art.
17. Finally, Ahlf provides no useful qualitative information about the final surface properties. Was the polished surface highly reflective, mirror-like, chrome-like, dark, machine line free, etc? Ahlf only points out that “Unaided visual inspection revealed metallic crystals in the casting's surface, and microscopic examination of the surface revealed clearly defined graphite flakes”. This leads to a myriad of questions, such as was he seeing metallic crystals and graphite flakes, or manganese phosphate crystals filling in the recessed areas of the grind lines of the original 180-grit surface giving the appearance of a smooth surface? Were the “metallic crystals” the shiny metal peaks protruding through a

dark manganese phosphate coating? The insufficient disclosure of Ahlf prevents one of ordinary skill in the art from knowing the answers to these basic questions.

18. In attempting to duplicate the Ahlf invention, the following passage from Ahlf at Col. 1, line 62 to Col. 2, line 11 is of particular relevance:

In practicing the invention, the metal surface is wetted with a solution of a compound which is known to rapidly oxidize the surface metal and to form a friable, relatively insoluble conversion coating thereon which is relatively impervious to the solution. A conforming surface is rubbed against the wetted metal surface so as to abrade and thereby remove the friable coating, thereby exposing freshly bared surface metal to the solution.

Continued rubbing of the surfaces, accompanied by rewetting of the metal surface, if necessary, results in repetitive formation and removal of a conversion coating on the metal surface and, therefore, gradual wearing away of surface irregularities. Upon removal of all irregularities and washing of the surface, a smooth conversion coating remains on the surface. Such a coating is highly desirable in many instances where the surface is to be used in a bearing application.

19. In essence, the polishing process of this invention is removing one layer of atomic iron at a time. The phosphating solution reacts with the surface layer of iron atoms to form a soft coating. This soft coating is easily removed by rubbing, and fresh chemistry is allowed to react with the newly exposed layer of iron. Therefore, the stock removal process is limited by the reaction of the manganese phosphate solution with the iron atoms. Therefore, if it could be shown dissolution of the iron in the acidic manganese phosphating solution is the primary method of stock removal, then Ahlf would therefore be claiming results that it did not actually accomplish.

Dissolution of a cast iron surface will result in the undesirable pitting and etching of

the cast iron surface even though it can reduce the effect of machine/grind lines. This will be discussed further below.

20. When I attempted to duplicate Example 1 in which Ahlf was attempting to polish "an iron casting with a flat face previously ground by a wheel of 180 grit", I did not produce the reported result. Gray cast iron samples were belted with a 3M Trizact 180 belt. The specimens had a starting surface with an  $R_a = 0.63\text{-}0.73 \mu\text{m}$  and  $R_{max} = 6.5\text{-}9.7 \mu\text{m}$ . I used a Buehler Polishing Cloth (4" PSA (69-3105 TEXMET 1000)), which covered an Aluminum lap from Buehler. The spindle speed was 1620 rpm. The cloth was saturated with AEROCOTE #4 at 100%. At the end of 10 seconds, the surface roughness was again measured. The  $R_a = 0.64 \mu\text{m}$  and the  $R_{max} = 5.55 \mu\text{m}$ . The belted lines were still visible. Therefore, it was concluded that essentially there was little if any polishing in the 10-second interval. The test was repeated at a concentration of 12.5 v/v%. At the end of 10 seconds, the  $R_a = 0.64 \mu\text{m}$  and the  $R_{max} = 10.3 \mu\text{m}$ , and after two minutes the  $R_a = 0.56 \mu\text{m}$  and the  $R_{max} = 4.88 \mu\text{m}$ . Belting lines were still visible.
19. Ahlf teaches that stock is removed from a workpiece by reacting the surface layer of iron with manganese phosphate to produce a softer surface. This softer surface (or conversion layer as described in my application) can be removed easier since it is softer than the basis metal cast iron. The rate of stock removal is therefore dependent on the rate of chemical reaction at the surface and the rate and effectiveness of rubbing off the softer layer.
20. In the well known book on phosphating metals, *The Phosphating of Metals* by Werner Rausch, page 77, a steel sheet is immersed in a manganese phosphate bath using nitrate as an accelerator at 95 °C. See Appendix 6. Photomicrographs are taken of the phosphating

process after 1, 10, 30, 100, 300, and 1000 seconds. At this elevated temperature, manganese phosphating occurs at a much faster rate than at the ambient temperature disclosed in Ahlf. Note, however, that it takes as long as 30 seconds to get a uniform coating. Ahlf, however, claims that the surface is smoothed in only 10 seconds at ambient temperature. The photographs also clearly show that etching (dissolution) is the primary process occurring early in the process. Pitting is observed in the photographs taken at 1 and 10 seconds.

21. A recent technical article entitled *Anti-Peeling Rolling Bearing with Manganese Phosphate Coating* by Y. Asai, N. Motohashi and Y. Sakaki in *KOYO Engineering Journal English Edition* No. 156E (2000) on page 17 reconfirms that dissolution is the initial mechanism, stating that “The iron of the surface base metal is dissolved during the initial manganese phosphate coating process, forming pits in the surface of the base metal. These pits are arranged at moderate size, depth and density.”
22. In fact, one of the references cited against Ahlf substantiates the slowness of this reaction. See Appendix 7, page 105 of *The Chemical Surface Treatment of Metals*: “Manganese phosphate solutions yield coating of equally good protective value but they too suffer from the disadvantages that the phosphating time is relatively long due to their slow rate of attack on the steel, and iron builds up in the solution.”
23. There is therefore strong technical evidence that dissolution—and not the friable phosphate coating mechanism described in Ahlf—occurred during the first 10 seconds. Dissolution will not lead to the smooth surface described in my application.

24. NALCO confirmed the fact that manganese phosphating occurs only at higher temperatures of approximately 90 °C. At ambient temperature dissolution rather than phosphating is the predominant reaction on the metal. Yet Ahlf states at Col. 4, lines 22-24, that "Each of the above examples was conducted at room temperature, and negligible temperature effects were noted."
25. One prior art reference to Ahlf discusses the *Cold phosphating processes*. See Appendix 8, page 107 of The Chemical Surface Treatment of Metals, noting that "Cold phosphating solutions contain zinc phosphate as their main constituent together with powerful accelerators. In some cases mixtures of zinc and manganese phosphates are used"
26. Realizing that Ahlf did not use a zinc phosphating solution, but a manganese phosphating solution, these cold phosphate solutions are still relatively slow in comparison with the 10 seconds required to polish the cast iron sample in Ahlf's Example I. Again, see Appendix 8, page 107 of The Chemical Surface Treatment of Metals, which states that "Depending on the type of bath and the accelerator used, a coating thickness of about 3  $\mu$  is obtained in 3 minutes and a 6  $\mu$  coating is formed in about 10 minutes."
27. I ran an experiment in which rectangular specimens having approximate dimensions of 50 mm x 25 mm x 4 mm were cut from gray cast iron and machined to a 180-grit finish. A 12 v/v% aqueous solution of AEROCOTE #4 was prepared since this was the recommended concentration for this product. The surface of the specimen was covered with this solution and observed at intervals of 10, 30 and 60 seconds. Vigorous evolution of gas was observed at each of these intervals. The test was repeated using 100%

AEROCOTE #4 with the same results. See Appendix 9. For all of the testing a very light coating of manganese phosphate was observed on the surface. The continuous degassing demonstrated that the surface was not completely covered with manganese phosphate. This supports the findings of Rausch and NALCO, and directly controverts Ahlf, as the mechanism of metal removal is dissolution.

28. Equally important is that after 60 seconds, there is only a very lightly darkened surface, showing again that no significant phosphating is occurring. Therefore, the stock removal must be a result of dissolution rather than the desired mechanism of creating a friable coating on the surface of the metal, removing it by rubbing, and reforming it again, and continuing the process until the roughened surface is polished smooth. This experimental work confirms the writing of Rausch and NALCO again, and directly controverts the teachings of Ahlf.
29. It is possible that partial smoothing of Ahlf's 180-grit surface of cast iron occurred by a dissolution process. Such a process is referred to as "chemical polishing" and is well documented in the literature.
30. At ambient conditions, a manganese phosphating process involves dissolution rather than phosphating, i.e., the chemistry chosen is inappropriate for the invention to work. Appendix 10 shows a specimen of cast iron finished with a 180-grit surface having a surface roughness of an  $R_a \approx 0.68 \mu\text{m}$ . After immersion in manganese phosphate solution (NALCO AEROCOTE #4) at full strength gas continues to evolve from the surface even after 30 minutes. The surface darkened considerably from the phosphate coating and the

machine lines became diffuse. After rubbing dry with a paper towel the surface roughness was measured to have an  $R_a \approx 0.43 \mu\text{m}$ . Since gas continued to be evolved even after 30 minutes, this coating cannot be functioning according to Ahlf's description. Ahlf states at Column 2, lines 44-53 that: "Many solutions are known to be capable of forming metal conversion coatings. Each of these solutions may be utilized in the present invention, and reference to specific examples is not to be construed as unnecessarily limiting the invention. The most effective solutions are those which, when in contact with metal, form a friable coating on the metal which is relatively impervious to the solution. The impervious nature of such a coating prevents further contact of the solution with surface metal, thereby slowing the rate of surface oxidation." Obviously, the manganese-iron phosphate complex does not form an impervious coating to the solution in the 10 second interval as described in Example 1, and dissolution must be the primary mechanism of line removal.

31. The Gedanke Experiment. Let us consider the following hypothetical experiment. Assume for the sake of example only that the Ahlf manganese-iron complex formed a uniform coating 100 times faster than the rate given in the Rausch reference (i.e., 30sec/100sec or approximately 0.30 second) on the surface of the cast iron. It therefore takes 0.30 seconds to remove one atomic layer of iron. For a 180-grit finished surface, the distance from the highest peak to the lowest valley, i.e.,  $R_z = 223 \mu\text{in.}$ , would be approximately 0.0005 cm. See Appendix 11. An elementary calculation shows that this thickness of stock removed required to achieve a smooth surface corresponds to

approximately 22,000 layers of iron atoms. See Appendix 12. Since according to the invention as described, material removal occurs by one atomic layer at a time. Thus approximately 1.8 hours is required to remove the 0.0005 cm of stock which is equivalent to 22,000 layers of iron atoms. This is over 650 times longer than the 10 seconds claimed by the invention to polish the surface. Therefore, it can be theoretically shown that the stock removal rate of Example 1, must be occurring by another process than that what is actually described in Ahlf. One alternative process that can occur at this rate is dissolution, which is not the mechanism claimed in the patent.

32. Concluding my analysis of Example 1, Ahlf did not teach how to carry out his invention, and in fact appears to have actually dissolved cast iron and/or smeared the soft cast iron material to a “smooth” surface. Had Ahlf used hardened steel and/or conducted a control test without any manganese-iron phosphate complex, he would have realized his fallacy. Therefore, the teachings of Ahlf are not applicable to my invention.
33. When I attempted to duplicate Example 2, I did not produce the reported result. Again, it should be noted that there are many numerous aluminum alloys, and Ahlf failed to identify the alloy of the rotary compressor end housings used in his study. (See Appendix 13.) Therefore, I chose to use 6061 because it was readily available both now and at the time of Ahlf’s patent. A 180-grit 3M Trizact Belt was used to impart a surface finish having an  $R_a = 1.38 \mu\text{m}$  and  $R_{\max} = 9.4 \mu\text{m}$  to two flat 6061 Aluminum test pieces. The roughened surfaces of the test pieces were wetted with the dichromate solution described in Ahlf and were gently rubbed together by hand with the grind lines perpendicular to each other. The surfaces were kept wet as needed. After 8 minutes of rubbing, particles were observed, indicating that the surface was being smoothed by abrasion of the peaks

of the roughened surfaces. The final surface has an  $R_a = 0.53-1.10 \mu\text{m}$ , and the  $R_{\max} = 4.88-7.95 \mu\text{m}$ . See Appendix 14.

34. The experiment was repeated again using only water to wet the surfaces. After 8 minutes of rubbing, particles were observed, indicating that the surface was being smoothed by abrasion of the peaks of the roughened surfaces. The final surface has an  $R_a = 0.51-0.92 \mu\text{m}$ , and the  $R_{\max} = 4.98-7.5 \mu\text{m}$ . Again metal particles were observed indicating that the process of smoothing was merely an abrading phenomenon, and not by the mechanism described in Ahlf. See Appendix 15. This is in sharp contradiction to Ahlf's statement at Col. 4, lines 14-19 that "It is believed that aluminum oxide formed between the surface irregularities and was not abraded by the rubbing motion, but that aluminum oxide which formed on high spots was broken away by abrasion, exposing bare aluminum to the dichromate solution for further oxidation." Had Ahlf done a baseline test using water alone, Ahlf would have discovered that this was incorrect.
35. The first chemical treatment for aluminum was developed by Bauer and Vogel in 1915 (German Patent 423,758), and was an alkaline dichromate solution consisting of Potassium carbonate (25 g/L), Sodium carbonate (10 g/L), and Potassium dichromate (10 g/L) which is similar to the chemistry used by Ahlf. This process, however, was operated at 90-95 °C for 2-4 hours to produce a light grey to dark grey depending on the immersion time. See *Phosphating and Metals Pre-Treatment* by D. B. Freeman Page 111. Ahlf, however, claims that this chemistry produced an oxide coating at a high enough rate to smooth aluminum in a practical amount of time at ambient temperature. Yet the literature states that this is an extremely slow process. This supports the conclusion that the

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Declaration of Gary Sroka

smoothing of the aluminum was a result of abrasion and not the mechanism of the invention described in Ahlf.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Gary J. Sroka

Gary J. Sroka, Ph. D.

March 17, 2004

Date

**Appendix 1: *The Chemical Surface Treatment of Metals* ('540 prior art), page 101.**

#### PROCESSES

##### **Heavy metal phosphating processes for iron and steel**

Besides the temperature and degree of agitation of the solution, the type and concentration of the phosphating compounds also influence the growth of the coating. Their choice depends on the application and on the time available for the formation of the coating.

In general terms, the growth of the coating is influenced by the concentration of metal ions and of phosphate ions in the solution. The ratio of free to total phosphoric acid is of particular importance in this respect. Mixtures giving ratios which are of practical use have mainly been protected by patents. If too much free phosphoric acid is present, the iron will be attacked too vigorously and the time to precipitation of the salts required for the coating process becomes longer. As a result the coatings are thin and have less protective value. If the heavy metal ion concentration is too low, the coating process is unsatisfactory even in solutions which contain oxidising agents. Decrease in concentration of the phosphating medium itself also generally reduces the protective value of the coating.

##### *Specifications*

In DIN 50 942 the processes are classified according to the formation conditions in six groups, A to F. Processes A to C yield coatings about  $10 \mu$  (0.4 mil) thick while processes D to F are recommended for producing coatings which are less than  $5 \mu$  (0.2 mil) in thickness. The thicker coatings are used principally for machine components and for apparatus which is not subjected to any mechanical wear. Thin phosphate coatings are used for parts which are required to conform to accurate dimensional tolerances and for parts which are required to resist impact. A supplement to DIN 50 942 gives the processes and classes of process which are suitable for particular applications (see Table 14).

In this country the phosphating of iron and steel is subject to two official specifications, DEF 29 and B.S.3189. The former, which is the Ministry of Defence specification, divides phosphate coatings into three classes, viz.:

Class I. Manganese and/or iron processes with a coating weight of not less than 700 mg/sq ft.

Class II. Zinc processes with a coating weight of not less than 400 mg/sq ft.

Class III. Light weight coatings of not less than 150 mg/sq ft—in special cases 50 - 150 mg/sq ft.

Class III are generally used for light gauge steel as preparation for painting. The specification lays down principles for rinsing, for coating high strength steels, for sealing the phosphate coating, and procedures for testing.

**Appendix 2: *The Chemical Surface Treatment of Metals* ('540 prior art), page 90.**

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and tertiary manganese and ferrous phosphates, the secondary phosphates being the more important. In the zinc phosphate baths on the other hand, coatings which are formed consist mainly of tertiary zinc phosphate together with variable amounts of secondary and tertiary iron phosphates. However, it is not the normal tertiary zinc phosphate which is formed but a basic phosphate which corresponds to the formula  $Zn_3(PO_4)_2 \cdot Zn(OH)_2$  and has a structure of the type of hydroxyapatite.

As the iron goes into solution and the pH value is shifted towards neutrality, a considerable quantity of sludge is formed in the bath. This contains di- and trivalent iron phosphates together with appreciable amounts of manganese- or zinc phosphates.

This means that pure manganese- and zinc phosphate baths have the following disadvantages: pronounced build-up of iron salts, considerable sludge formation and high consumption of chemicals. As the bath is operated, increasing amounts of iron phosphates are deposited in the coating and these reduce the corrosion resistance. The life of the baths is therefore relatively brief. Nor is it possible to regenerate the solution.

*Effect of additions of oxidising agents*

The acid phosphating solutions which contain oxidising agents behave very differently. In the presence of the oxidising agent, the nascent hydrogen is oxidised and also the ferrous ions formed by the reaction are oxidised to ferric ions. Consequently ferric phosphate is formed and precipitates as sludge. The result is that in these baths the iron content is stabilised and remains constant.

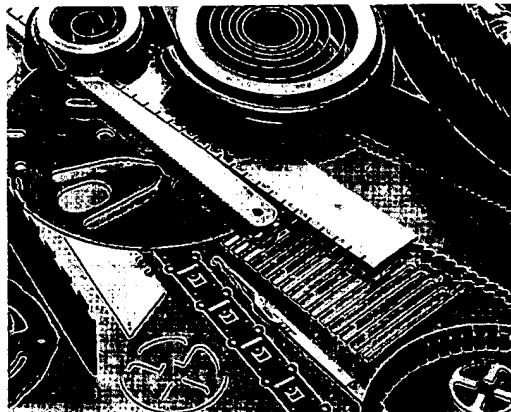
The manganese- or zinc phosphate concentration of this type of solution also remains approximately constant. Thus the composition of phosphating solutions containing oxidising agents remain relatively constant, which means that uniform coatings are produced. Moreover it is usually possible to regenerate the solutions by adding the correct amounts of the chemicals. Due to the difference in dissociation constants, the coatings produced in manganese phosphate solutions contain more iron than those formed in zinc phosphate baths.

*Factors determining rate of growth of coating*

The rate of growth of the coating is highest at the start of the process. It then decreases with the rate at which the anodic area is reduced and the cathodic area increased. The rate of growth of the coating, therefore, is proportional to the anodic area at any given time. From this it follows that

### Appendix 3: Metallurgy Fundamentals, Daniel A. Brandt & J. C. Warner, The Goodheart-Willcox Company, Inc., 1999

Chapter 5 What Is Steel? 81



**Figure 5-25.** Spring steel is made into many different shapes for a variety of applications other than conventional springs. (Wallace Barnes Steel, Barnes Group Inc.)

## Cast Iron

**Cast iron** is a material that uses iron as its primary ingredient. It contains 2% to 6% carbon and small amounts of silicon. Other alloying elements are also used. Bear in mind that "cast iron" and "iron" are two very different terms. Consider it a coincidence that the word *iron* is used in both names.

### How Steel and Cast Iron Differ

It is important to understand the difference between steel and cast iron. The difference can be described as follows. When steel is produced, the carbon that is added to the iron dissolves and disappears. This is similar to the dissolving of sugar in water. If you add a small amount of sugar to a glass of water, the sugar immediately dissolves and becomes invisible. If you add a little more sugar, the same thing happens. Eventually, if you add enough sugar, the water does not dissolve all of it. Some sugar precipitates out, and it becomes visible.

The same situation exists with iron and carbon in steel and cast iron. When carbon is added to iron, the carbon dissolves and

disappears. Eventually, if enough carbon is added, it precipitates out. Steel is iron with the carbon in solution, which occurs below 1.6 to 2% (the percentage varies in different types of steel). Cast iron is iron in which some of the carbon has precipitated out and appears as flakes (as in gray cast iron, the most common iron of the cast iron family) or little spheres (nodular iron). See Figure 5-26.

The effects of the precipitated carbon are both good and bad. The flakes provide a cushioning effect for iron when it receives high compression loads, Figure 5-27. This makes cast iron a very good material when vibration is present along with large compressive loads. See Figure 5-28.

On the other hand, gray cast iron is more brittle than steel, and it has very poor strength when stretched in tension, Figure 5-29. The precipitated flakes encourage the formation of cracks and cause breakage.



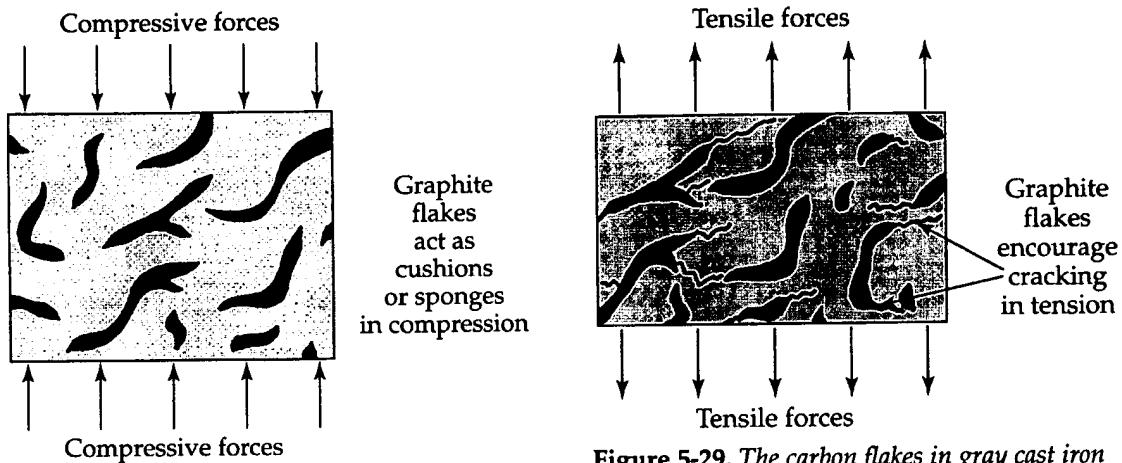
A



B

**Figure 5-26.** Cast iron crystals. A—In gray cast iron, carbon flakes tend to crystallize out of the iron. (General Motors Powertrain Group) B—The graphite flakes in this cast iron sample are very fine and can barely be recognized. The flakes are the tiny black lines that appear throughout the photograph. (Buehler Ltd.)

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**Figure 5-27.** Carbon flakes serve as a cushion for iron and protect it during compression.

**Figure 5-29.** The carbon flakes in gray cast iron make it weaker than pure iron in tension.



**Figure 5-28.** This precision tool grinder base absorbs vibration. Making the base from cast iron gives it a long service life. (Iron Castings Society)

Cast iron is very easy to machine. It is also easy to cast, due to the significantly low melting point relative to steel. This is a direct result of the higher carbon content of cast iron. Cast iron casting is also easier to control than steel casting.

### *Applications of Cast Iron*

Cast iron is used extensively for the frames of large equipment and machine tools, Figure 5-30. Its damping capacity and compressive strength make it very suitable for these applications. Because cast iron has very good resistance to wear, it is used for engine blocks, piston rings, brake drums, rolls, and crushers.

In architecture, cast iron is used for stair treads and lampposts. Cast iron is also used for manhole covers, furnace grates, and any other applications where its castability, machinability, damping characteristics, and compressive strength are of benefit.

### *Types of Cast Iron*

The following are the five basic types of cast iron (see Figure 5-31):

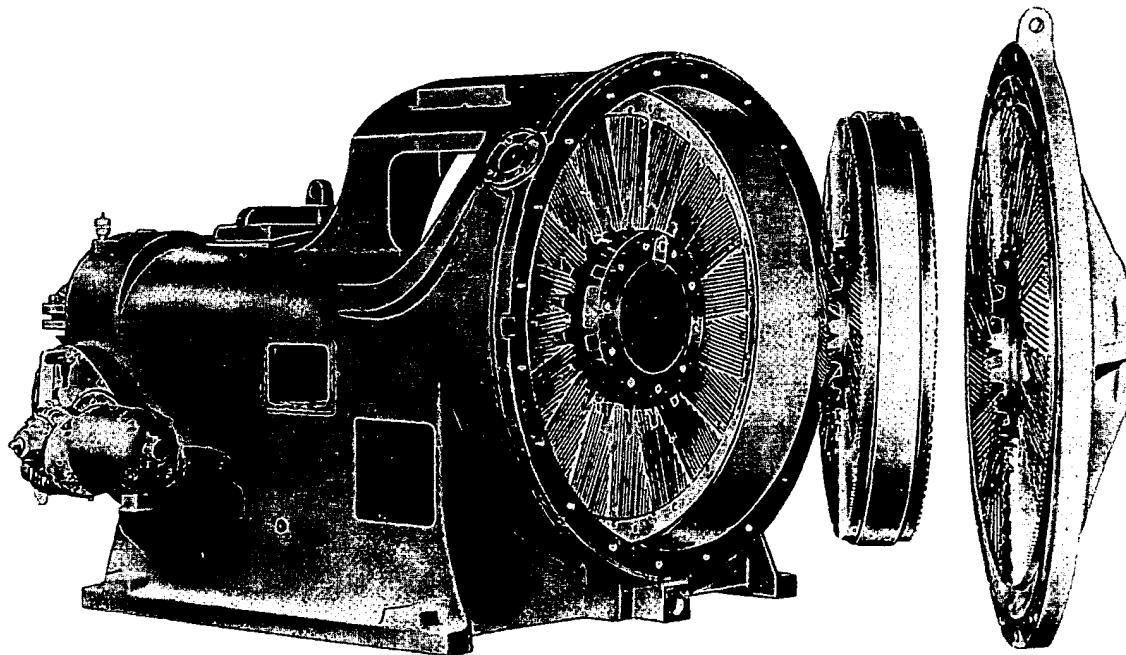
- Gray.
- White.
- Malleable.
- Ductile.
- Special alloy.

#### **Gray cast iron**

When people refer to a material as *cast iron*, but do not specify the type, chances are

Types of Cast Iron
• Gray (most common)
• White (most brittle)
• Malleable (higher quality)
• Ductile (higher quality)
• Special alloy (special properties)

**Figure 5-31.** This chart lists the five basic types of cast iron.



**Figure 5-30.** Iron castings are used extensively in paper mill equipment, such as this large pulp refiner. Cast iron meets rugged service and corrosion resistance requirements. (Iron Castings Society)

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they are talking about gray cast iron. *Gray cast iron* is the most widely used type of cast iron. In fact, there is more gray cast iron used than the other four types combined.

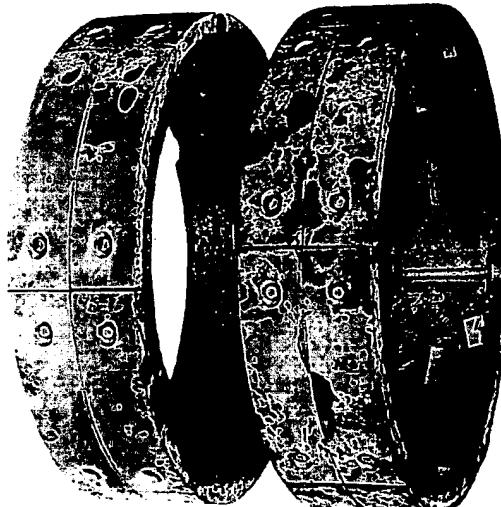
Although gray cast iron does not have some of the good qualities of ductile, malleable, or special alloy cast iron, it is considerably less expensive. The differences in cost and quality must be considered when a type of cast iron is chosen for a given application.

Gray cast iron is very hard and brittle, and it has relatively poor tensile strength due to the graphite flakes in its structure. However, it has excellent compressive strength and damping capacity, and it can be easily cast.

#### White cast iron

*White cast iron* is not used as extensively as gray cast iron because it is harder, more brittle, and more difficult to machine. It also has less impact strength.

The extreme hardness of white cast iron, however, makes it a valuable material for some applications. For example, white cast iron rolls, used in mills, need great hardness



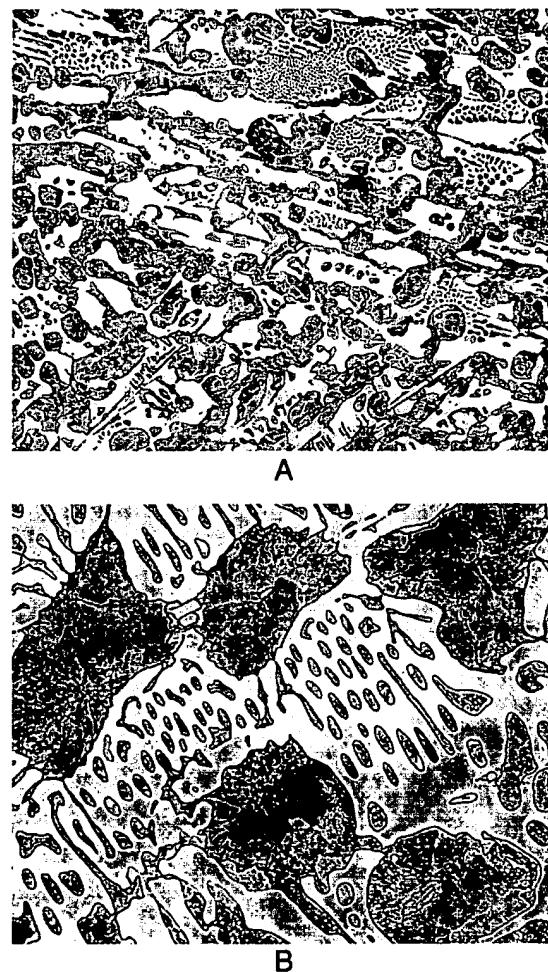
**Figure 5-32.** White cast iron is used in these muller tires because of its superior hardness and abrasion resistance. (Iron Casting Society)

to break up stone and other materials. See Figure 5-32. White cast iron is also produced as an intermediate step in the production of malleable cast iron.

When white cast iron is observed under a microscope, it looks much different from gray cast iron. See Figure 5-33.

#### Malleable cast iron

*Malleable cast iron* has several special properties that make it superior to both gray cast



**Figure 5-33.** Microscopic views of white cast iron. A—Magnification is 100X. B—Magnification is 400X. (LECO Corporation)

iron and white cast iron. Malleable cast iron has more tensile strength, ductility, and impact strength. It also costs more than gray cast iron or white cast iron. The table in Figure 5-34 compares the properties of the various types of cast iron.

Malleable cast iron is made from white cast iron. The white cast iron is heated extensively at high temperatures to refine it. Eventually, carbides break down into carbon and free iron. The carbon collects in small, roughly spherical particles known as *temper carbon particles*. The formation of these particles causes malleable cast iron to become more ductile and workable, without sacrificing high compressive strength. Common applications for malleable cast iron are shown in Figure 5-35.

#### Ductile cast iron

*Ductile cast iron* is sometimes referred to as *nodular cast iron* because its graphite particles are shaped like tiny spheres (or nodules). Unlike the temper carbon particles in malleable cast iron, the nodules in ductile cast iron are precipitated directly from the liquid iron by treatment with magnesium.

Ductile cast iron, as its name implies, has great ductility. Its tensile strength is comparable to that of malleable cast iron, Figure 5-34. The price of ductile cast iron has become more competitive, and it is replacing gray cast iron in many applications. Some typical uses of ductile cast iron are shown in Figure 5-36.

#### Special alloy cast iron

Most cast iron has a very basic alloy content. It primarily contains just carbon and silicon as its alloys. A number of types of *special alloy cast iron* have been developed for specific applications.

A few grades of special alloy cast iron contain high percentages of nickel, copper, chromium, and other alloys. Nickel, copper, and chromium produce good corrosion resistance and good chemical resistance to acids.

Properties of Cast Iron				
	Gray	White	Malleable	Ductile
Weight lbs/in <sup>3</sup>	.25-.27	.27-.28	.26-.27	.25-.27
Tensile Strength psi × 10 <sup>3</sup>	20-70	20-50	60-120	60-120
Compressive Strength psi × 10 <sup>3</sup>	100- 170	100- 150E	200-290	120-300
Impact Strength V-Notched Charpy ft-lb	Low	3-10	14-17	2-30
Hardness BHN	140- 290	300- 580	110-270	140-330
Modulus of Elasticity psi × 10 <sup>6</sup>	12-20	Low	25-28	18-25
Coefficient of Thermal Expansion in./in. °F × 10 <sup>-6</sup>	6	5	6-8	6-10

Figure 5-34. A comparison of the properties of different types of cast iron.

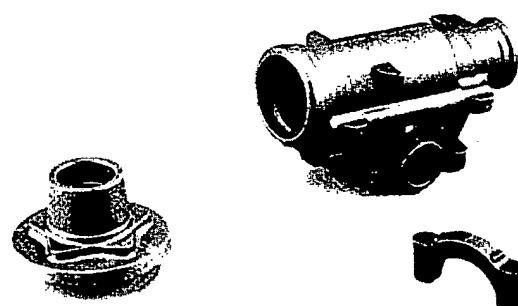
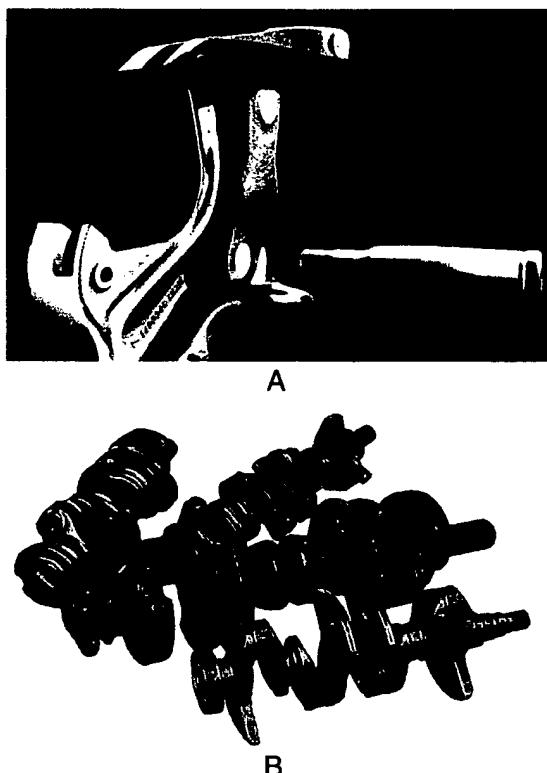


Figure 5-35. Malleable cast iron is used for applications requiring high ductility and compressive strength. (General Motors Powertrain Group)

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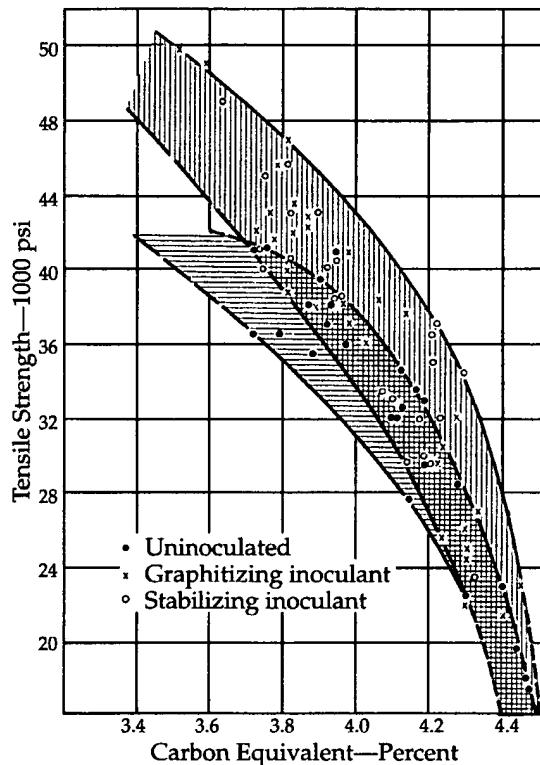
**Figure 5-36. Ductile cast iron applications.**  
 A—The wheel spindle and support shown are ductile cast iron parts. B—Automotive crankshafts are typically ductile cast iron parts.  
 (General Motors Powertrain Group)

Other special alloy cast irons have been developed that have greater strength and better high-temperature properties, Figure 5-37. Special alloy cast iron is used in cylinders, pistons, piston rings, and turbine stator vanes, Figure 5-38.

## Wrought Iron

Wrought iron is very different from cast iron. *Wrought iron* is almost pure iron; it has very little carbon in its composition, Figure 5-5.

Wrought iron has very low strength and hardness, since it contains little carbon. However, it is very ductile and resistant to corrosion. Before 1860, wrought iron was the most



**Figure 5-37. The addition of small quantities of alloys to cast iron (inoculation) improves its properties. This graph shows the influence of alloys on the tensile strength of cast iron. (Iron Castings Society)**

important structural metal available. However, due to advances brought about by metallurgical research, wrought iron has been widely replaced as a structural material.

The key asset for wrought iron today is good corrosion resistance. Many fibrous stringers of slag are distributed throughout wrought iron. If corrosion attacks the iron, the deterioration proceeds only until it meets a slag stringer. The corrosion stops there, and forms a protective coating. The slag then becomes a barrier against further corrosion.

A microscopic view of slag stringers is shown in Figure 5-39. The slag contains considerable amounts of silicon. A typical chemical makeup of wrought iron is shown in Figure 5-40.

**Appendix 4: *The Chemical Surface Treatment of Metals* ('540 prior art), page 95.**

**INFLUENCE OF METAL SURFACE**

particularly if the initial reaction is the action of phosphoric acid on steel. Good results are therefore obtained on electrolytic iron. The condition of the basis metal surface mainly effects the growth of nuclei. On the other hand, no effect of the orientation of the basis metal on the structure of the coating has been observed.

The condition of the surface has a far stronger and more lasting influence in the slow phosphating processes than in those which contain oxidising agents. This can be explained by the fact that in the presence of oxidising agents the local cells are polarized, resulting in a considerable increase in the rate of nucleation and thus the number of nuclei compared with coatings produced in solutions without additives. Thus in the absence of oxidising agents, the tendency of the steel to form a phosphate coating decreases with increasing content of alloying constituents.

In order to be able to coat difficult alloy steels of this type satisfactorily, it has been suggested that the steel be provided with a coating of pure iron before phosphating. Alternatively an extremely thin coating of zinc, less than 0.0001 in thick, may be electrodeposited.

***Carbon content of steel***

Some data are available about the influence of increasing carbon content in steel on phosphating in manganese phosphate baths. In investigating normalised steels with carbon contents of 0.12, 0.29, 0.62 and 0.73 per cent, it was observed that, with increasing pearlite content, the crystal size of the phosphate coating increased. This has been ascribed to the fact that comparatively few nuclei are formed on the islets of pearlite. W. Machu<sup>(22)</sup> has carried out a similar study using a zinc phosphate solution containing nitrate. In these experiments, it was observed that phosphate coatings on ground carbon steels showed a uniformly smaller free pore area than similar coatings on electrolytic iron although there was no visible enlargement of the grains. From this, it can be concluded that the carbon content will not exert any significant influence on the growth of phosphate coatings from accelerated solutions which contain oxidising agents.

***Other alloy constituents***

From the results of other investigations which have been carried out on phosphating solutions which contain oxidising agents, it can be concluded that alloy constituents have only a minor influence and that there are no difficulties in phosphating low-alloy steels. Even on steels with higher contents of alloying constituents and carbon, uniform coatings are produced in

**Appendix 5: Chart Showing the Correlation between the Brinell Hardness Number and the Rockwell Hardness Number C-Scale (HRC). Taken from *Hardness Testing*, edited by Howard E. Boyer, ASM International, Metals Park, OH 44073, 1987**

**Appendix 1 Hardness Conversion Tables / 153**

**Approximate equivalent hardness numbers for Brinell hardness numbers for steel(a)**

Brinell indentation diam., mm	Brinell hardness No. (b), 3000-kg load			Rockwell hardness No.						Rockwell superficial hardness No., diamond indenter				Knoop hardness No., 50.0-kg load and greater	Schleif-schleif hardness No.
	Standard ball			Tungsten carbide ball			A scale, 60-kg load	B scale, 100-kg load	C scale, 150-kg load	D scale, 100-kg load	15N, 30N, 45N	30N, 45N	45N, 60N		
	Vickers hardness No.	diamond indenter	1/16-in. diam ball	diamond indenter	1/16-in. diam ball	diamond indenter	1/16-in. diam ball	diamond indenter	1/16-in. diam ball	diamond indenter	1/16-in. diam ball	diamond indenter	1/16-in. diam ball		
2.25	...	(745)	840	84.1	...	65.3	74.8	92.3	82.2	72.2	852	91	...	...	...
2.30	...	(712)	783	83.1	...	63.4	73.4	91.6	80.5	70.4	808	...	...	...	...
2.35	...	(682)	737	82.2	...	61.7	72.0	91.0	79.0	68.5	768	84	...	...	...
2.40	...	(653)	697	81.2	...	60.0	70.7	90.2	77.5	66.5	732	81	...	...	...
2.45	...	627	667	80.5	...	58.7	69.7	89.6	76.3	65.1	703	79	...	...	...
2.50	...	601	640	79.8	...	57.3	68.7	89.0	75.1	63.5	677	77	...	...	...
2.55	...	578	615	79.1	...	56.0	67.7	88.4	73.9	62.1	652	75	...	...	...
2.60	...	555	591	78.4	...	54.7	66.7	87.8	72.7	60.6	626	73	...	...	...
2.65	...	534	569	77.8	...	53.5	65.8	87.2	71.6	59.2	604	71	...	...	...
2.70	...	514	547	76.9	...	52.1	64.7	86.5	70.3	57.6	579	70	...	...	...
2.75	{ (495)	...	519	76.7	...	51.6	64.3	86.3	69.9	56.9	571	69	...	...	...
	495	528	76.3	...	51.0	63.8	85.9	69.4	56.1	558	68	...	...	...	...
2.80	{ (477)	...	516	75.9	...	50.3	63.2	85.6	68.7	55.2	545	66	...	...	...
	477	508	75.6	...	49.6	62.7	85.3	68.2	54.5	537	66	...	...	...	...
2.85	{ (461)	...	495	75.1	...	48.8	61.9	84.9	67.4	53.5	523	63	...	...	...
	461	491	74.9	...	48.5	61.7	84.7	67.2	53.2	518	63	...	...	...	...
2.90	{ (444)	...	474	74.3	...	47.2	61.0	84.1	66.0	51.7	499	61	...	...	...
	444	472	74.2	...	47.1	60.8	84.0	65.8	51.5	496	61	...	...	...	...
2.95	429	429	73.4	...	45.7	59.7	83.4	64.6	49.9	476	61	...	...	...	...
3.00	415	415	72.8	...	44.5	58.8	82.8	63.5	48.4	459	59	...	...	...	...
3.05	401	401	72.0	...	43.1	57.8	82.0	62.3	46.9	441	58	...	...	...	...
3.10	388	388	71.4	...	41.8	56.8	81.4	61.1	45.3	423	56	...	...	...	...
3.15	375	375	70.6	...	40.4	55.7	80.6	59.9	43.6	407	54	...	...	...	...
3.20	363	363	70.0	...	39.1	54.6	80.0	58.7	42.0	392	52	...	...	...	...
3.25	352	352	69.3	(110.0)	37.9	53.8	79.3	57.6	40.5	379	51	...	...	...	...
3.30	341	341	68.7	(109.0)	36.6	52.8	78.6	56.4	39.1	367	50	...	...	...	...
3.35	331	331	68.1	(108.5)	35.5	51.9	78.0	55.4	37.8	356	48	...	...	...	...
3.40	321	321	67.5	(108.0)	34.3	51.0	77.3	54.3	36.4	345	47	...	...	...	...
3.45	311	311	66.9	(107.5)	33.1	50.0	76.7	53.3	34.4	336	46	...	...	...	...
3.50	302	302	66.3	(107.0)	32.1	49.3	76.1	52.2	33.8	327	45	...	...	...	...
3.55	293	293	65.7	(106.0)	30.9	48.3	75.5	51.2	32.4	318	43	...	...	...	...
3.60	285	285	65.3	(105.5)	29.9	47.6	75.0	50.3	31.2	310	42	...	...	...	...
3.65	277	277	64.6	(104.5)	28.8	46.7	74.4	49.3	29.9	302	41	...	...	...	...
3.70	269	269	64.1	(104.0)	27.6	45.9	73.7	48.3	28.5	294	40	...	...	...	...
3.75	262	262	63.6	(103.0)	26.6	45.0	73.1	47.3	27.3	286	39	...	...	...	...
3.80	255	255	63.0	(102.0)	25.4	44.2	72.5	46.2	26.0	279	38	...	...	...	...
3.85	248	248	62.5	(101.0)	24.2	43.2	71.7	45.1	24.5	272	37	...	...	...	...
3.90	241	241	61.8	100.0	22.8	42.0	70.9	43.9	22.8	265	36	...	...	...	...
3.95	235	235	247	61.4	99.0	21.7	41.4	70.3	42.9	21.5	259	35	...	...	...
4.00	229	229	241	60.8	98.2	20.5	40.5	69.7	41.9	20.1	253	34	...	...	...
4.05	223	223	234	...	97.3	(19.0)	...	...	...	247	33	...	...	...	...
4.10	217	217	228	...	96.4	(17.7)	...	...	...	242	33	...	...	...	...
4.15	212	212	222	...	95.5	(16.4)	...	...	...	237	32	...	...	...	...
4.20	207	207	218	...	94.6	(15.2)	...	...	...	232	31	...	...	...	...
4.25	201	201	212	...	93.7	(13.8)	...	...	...	227	30	...	...	...	...
4.30	197	197	207	...	92.8	(12.7)	...	...	...	222	30	...	...	...	...
4.35	192	192	202	...	91.9	(11.5)	...	...	...	217	29	...	...	...	...
4.40	187	187	196	...	90.9	(10.2)	...	...	...	212	28	...	...	...	...
4.45	183	183	192	...	90.0	(9.0)	...	...	...	207	28	...	...	...	...
4.50	179	179	188	...	89.0	(8.0)	...	...	...	202	27	...	...	...	...
4.55	174	174	182	...	88.0	(6.7)	...	...	...	198	26	...	...	...	...
4.60	170	170	178	...	87.0	(5.4)	...	...	...	194	26	...	...	...	...
4.65	167	167	175	...	86.0	(4.4)	...	...	...	190	25	...	...	...	...
4.70	163	163	171	...	85.0	(3.3)	...	...	...	186	25	...	...	...	...
4.75	159	159	167	...	83.9	(2.0)	...	...	...	182	24	...	...	...	...
4.80	156	156	163	...	82.9	(0.9)	...	...	...	178	24	...	...	...	...
4.85	152	152	159	...	81.9	...	...	...	...	174	23	...	...	...	...
4.90	149	149	156	...	80.8	...	...	...	...	170	23	...	...	...	...
4.95	146	146	153	...	79.7	...	...	...	...	166	22	...	...	...	...
5.00	143	143	150	...	78.6	...	...	...	...	163	22	...	...	...	...
5.10	137	137	143	...	76.4	...	...	...	...	157	21	...	...	...	...
5.20	131	131	137	...	74.2	...	...	...	...	151	20	...	...	...	...
5.30	126	126	132	...	72.0	...	...	...	...	145	19	...	...	...	...
5.40	121	121	127	...	69.8	...	...	...	...	140	19	...	...	...	...
5.50	116	116	122	...	67.6	...	...	...	...	135	18	...	...	...	...
5.60	111	111	117	...	65.4	...	...	...	...	131	17	...	...	...	...

*Note: Values in parentheses are beyond normal range and are given for information only.*

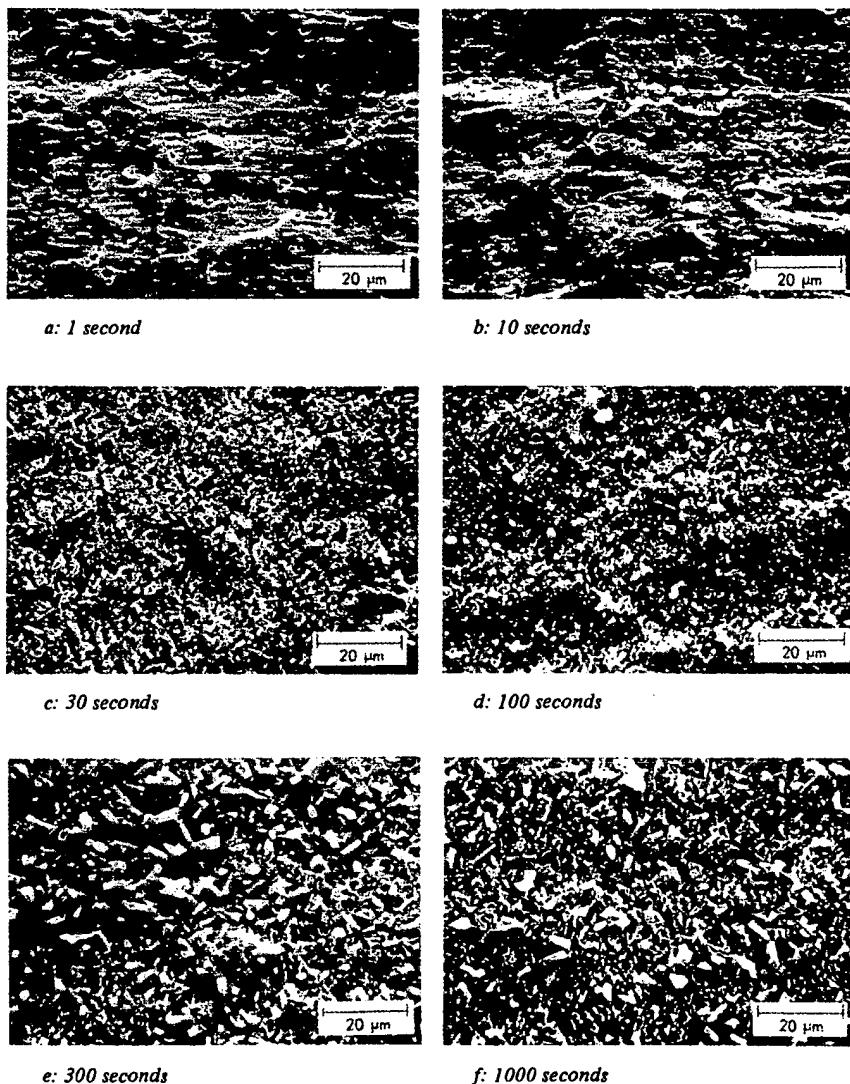
(a) For carbon and alloy steels in the annealed, normalized, and quenched and tempered conditions; less accurate for cold worked

**Appendix 6: *The Phosphating of Metals***, Dr. Werner Rausch, ASM International, Metals Park, OH, English Language Version published in 1990

**Photomicrographs of Manganese Phosphating at Various Time intervals.**

3.1 PHOSPHATE COATING PROCESSES

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*Fig. 35. Steel sheet, immersion phosphated with nitrate accelerated manganese phosphate bath for times as shown<sup>216</sup>*

**Appendix 7: *The Chemical Surface Treatment of Metals* ('540 prior art), page 105.**

**P R O C E S S E S**

Collardin Oberflächenchemie, Köln-Ehrenfeld	Deoxidine
	Duridine
	Granodine
	Lithoform
	Permadine
	Themoil-Granodine
Carl Dittmann & Co., Karlsruhe/Baden	Ferrophat
Farbwerke Hoechst AG, Frankfurt/Main	Atrament
Dr. Karnbach, Weinberger & Blume KG, Düsseldorf-Stockum	Phosphatol
Metallgesellschaft AG, Frankfurt/Main	Bonder
	Kaltbonder
	Parkerlösung
Pennsalt Chemicals	Pennsalt
W. L. Schwaab, Weingarten/Baden	Schwaabetaan-Calfos
Uecker KG	Uckro-Phosphat-Verfahren
VEB Galvanotechnik, Leipzig 05	GTL-Heissphosphat
	GTL-Kaltphosphat
Werner Zwez Fabrik für Metallchemie, Bergisch-Gladbach	Phosphavit-Schnell-phosphatierung

B.S. 3189, which is based on the Defence Specification, categorizes phosphate coatings as:

- Class A1. Heavy manganese and/or iron, not less than 700 mg/sq ft.
- Class A2. Heavy zinc, not less than 700 mg/sq ft.
- Class B. Medium zinc or other metal phosphate, not less than 400 mg/sq ft.
- Class C. Light zinc or other metal phosphate, 100 - 400 mg/sq ft.
- Class D. Extra light iron, 30 - 100 mg/sq ft.

The specification also specifies the rinsing procedure and lists the recommended concentrations of chromates in the final rinse, and tabulates the heat treatments to be given to high tensile steels. In addition, there is a section on inspection and testing of phosphate coatings.

The adoption of these specifications has led to a marked improvement in the standard of operation of the processes in industry generally.

*Composition of solutions*

The chief constituents of the phosphating solutions most used at present are zinc or manganese phosphates. Iron phosphate solutions have become almost obsolete due to the longer immersion times and higher operating temperatures which they require. Manganese phosphate solutions yield coatings of equally good protective value but they too suffer from the disadvantages that the phosphating time is relatively long due to their slow rate of attack on the steel, and iron builds up in the solution. This last factor results in the

**Appendix 8: *The Chemical Surface Treatment of Metals* ('540 prior art), page 107.**

**P R O C E S S E S**

*Cold phosphating processes*

As some addition agents do not withstand heating to the higher temperatures, special formulations have been developed which are capable of yielding good coatings at lower temperatures. Useful, uniform, fine grained and dense phosphate coatings can be obtained in a few minutes even at room temperature using the so called cold phosphating processes. The special advantages of cold phosphating are that the solution attacks the tank walls and equipment less rapidly, no steam is evolved, the equipment does not become encrusted, less energy is required and the solution is always ready for use without any time being needed for a heating up period.

Cold phosphating solutions contain zinc phosphate as their main constituent together with powerful accelerators. In some cases mixtures of zinc and manganese phosphates are used. Maintenance of the correct pH value is important as phosphoric acid is liberated during the coating process. As a result, the excess acid must be neutralised from time to time by adding caustic soda, zinc oxide or zinc or sodium carbonate. As the cold phosphating solutions have a relatively low rate of attack on the metal, the more difficult steels cannot be treated. In some cases, however, this disadvantage can be overcome by the use of a special pretreatment or the use of special operating conditions.

The coatings obtained in this way are generally a little lighter in colour and are finer grained than those produced by hot phosphating processes. There is, however, no difference in chemical composition. Depending on the type of bath and the accelerator used, a coating thickness of about  $3 \mu$  is obtained in 3 minutes and a  $6 \mu$  coating is formed in about 10 minutes. The corrosion resistance of this type of coating is similar to that obtained by hot phosphating.

*Spray processes*

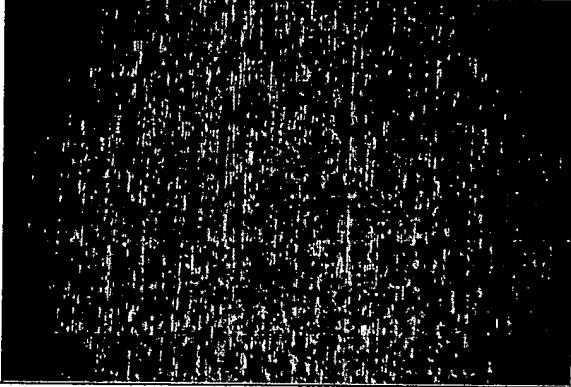
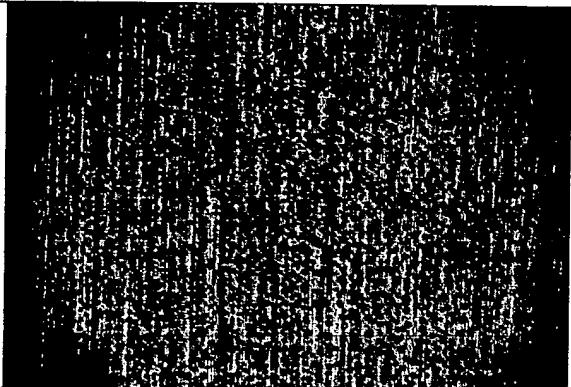
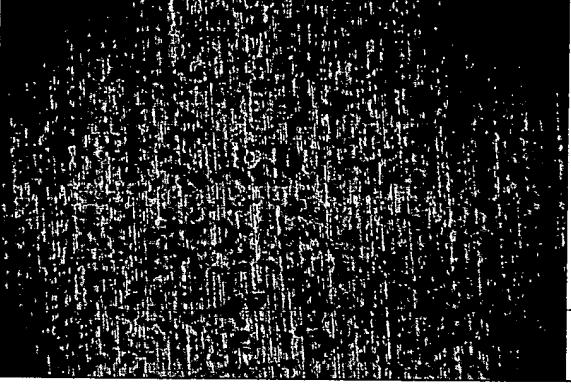
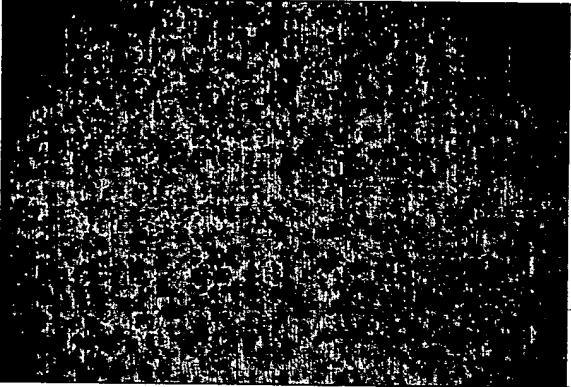
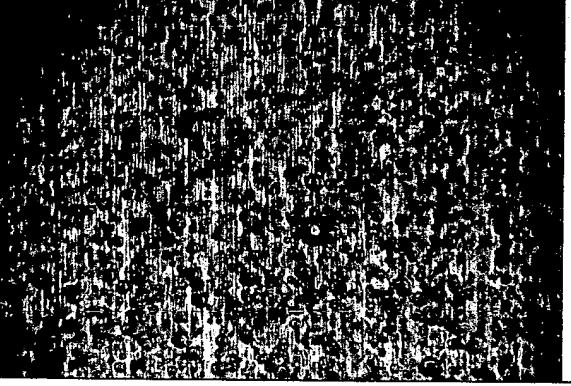
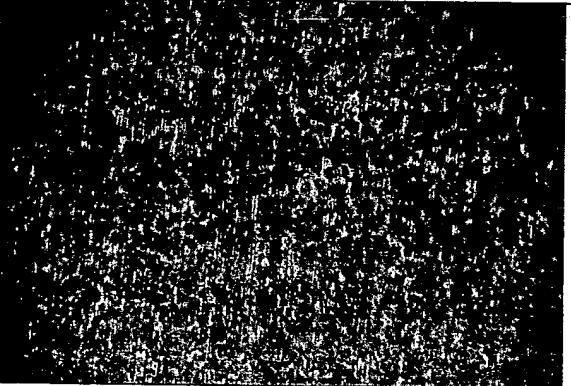
The phosphating process can also be accelerated by spraying the solutions on to the metal. Hot phosphating solutions are mainly used for this purpose. Due to the fact that the solution in contact with the basis metal is being completely and rapidly renewed the coatings are particularly fine grained. The treatment times are also relatively short.

*Plant<sup>(299-329)</sup>*

Plant and equipment has been designed for the operation of phosphating processes and some examples are shown in the accompanying illustrations. These are of either the immersion or spray type. Of special importance at the present time are also continuous strip plant and barrel automatics.

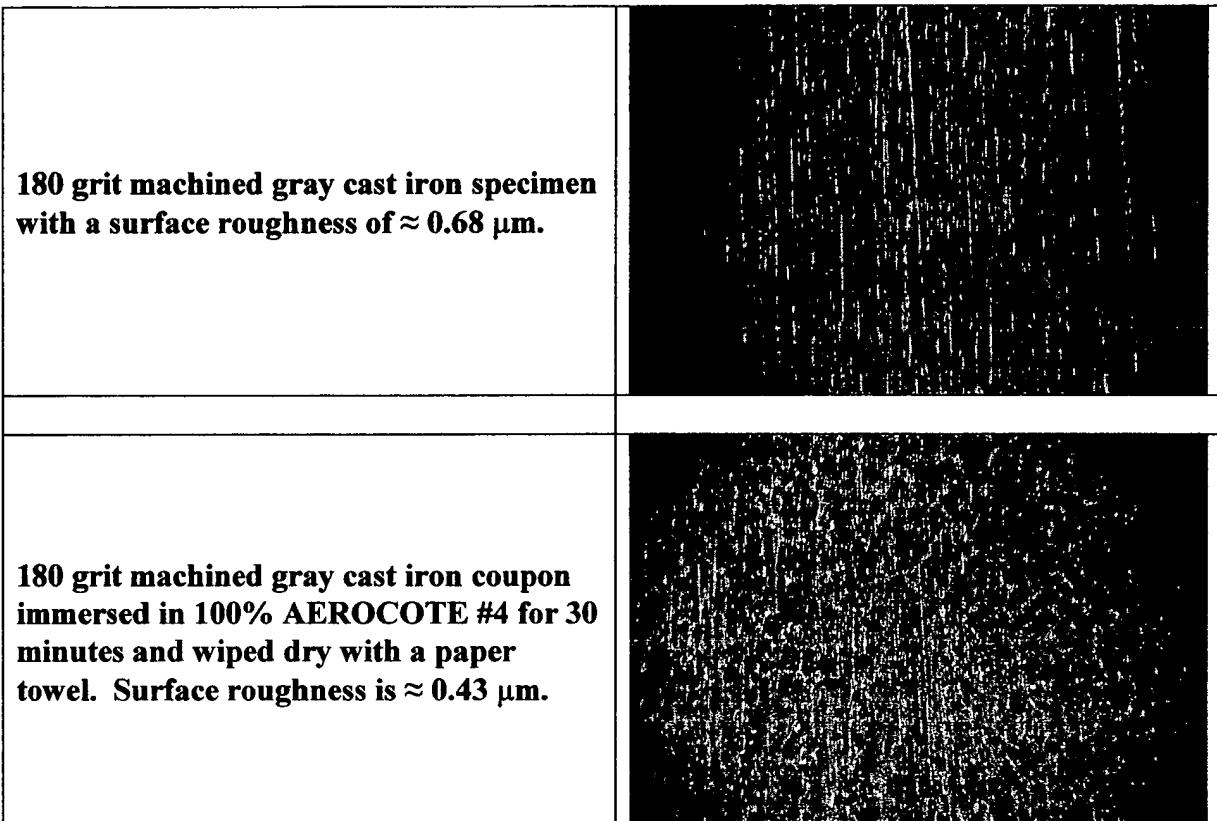
Serial No.: 10/071,533  
Confirmation No.: 1312  
Applicant: Michaud, et al.  
Atty. Ref.: 12350.0010.NPUS00  
Declaration of Gary Sroka

**Appendix 9:** Photomicrographs (10x) of 180 grit machined gray cast iron samples immersed in the two different concentrations of AEROCOTE #4 at intervals of 10 s, 30,s and 60 s intervals. Note bubbles covering the entire surface of all samples.

Time	AEROCOTE #4 Concentration	
	12.5 v/v%	100%
10 s		
30 s		
60 s		

Serial No.: 10/071,533  
Confirmation No.: 1312  
Applicant: Michaud, et al.  
Atty. Ref.: 12350.0010.NPUS00  
Declaration of Gary Sroka

**Appendix 10:** Photomicrographs (10X) comparing a 180-grit machined specimen at start of experiment with the specimen after being immersed in the manganese phosphate solution for 30 minutes. Note that the phosphate specimen appears somewhat smoother.



Serial No.: 10/071,533  
 Confirmation No.: 1312  
 Applicant: Michaud, et al.  
 Atty. Ref.: 12350.0010.NPUS00  
Declaration of Gary Sroka

Appendix 11: Surface roughness profile showing the amount of stock required for smoothing a 180-grit surface.

## ***REM Chemicals, Inc.***

Date of Profile: 02.20.04

Company: Patent Response

Technician: Lane Winkelmann

Bemerkung: 30 min 100%

Aerocote

#4Baseline Ground

Trizact 180g

HOMMELWERKE

Turbo Datawin-NT 1.44

Measuring conditions

Pick-up type

Measuring range

Assessment length

Lc (Cut Off)

02.20.04

TK300

3200  $\mu$ "

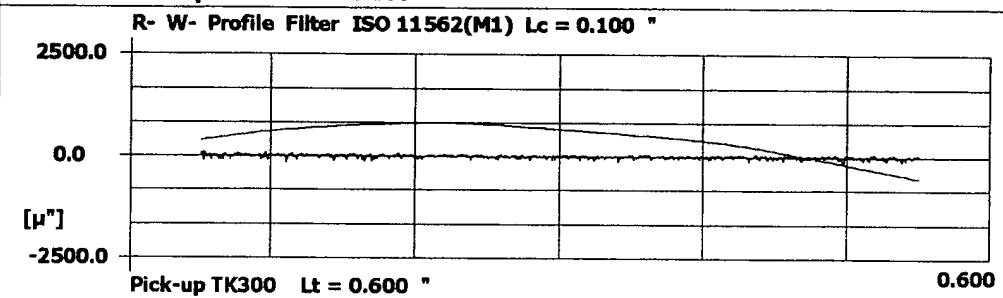
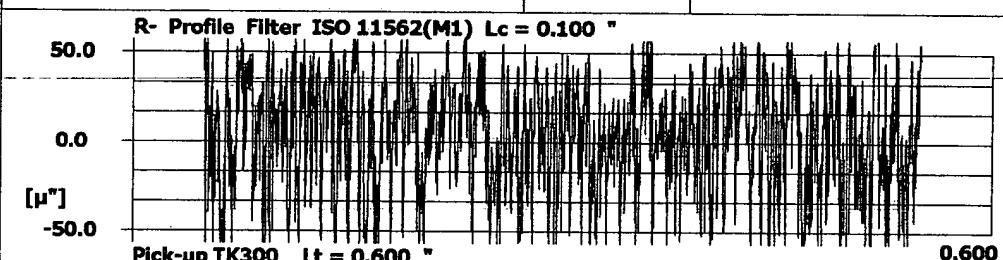
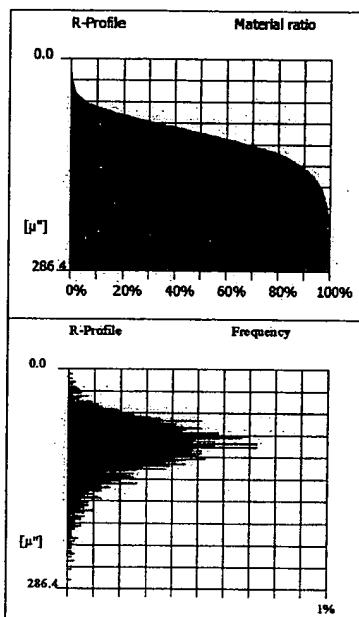
0.600 "

0.100 "

R <sub>t</sub>	286.42 $\mu$ m
R <sub>max</sub>	286.42 $\mu$ m
R <sub>z</sub>	223.05 $\mu$ m
R <sub>a</sub>	26.67 $\mu$ m
R <sub>p</sub>	107.48 $\mu$ m
R <sub>Sm</sub>	0.002 in
R <sub>k</sub>	80.31 $\mu$ m
R <sub>pk</sub>	19.89 $\mu$ m
R <sub>vk</sub>	53.15 $\mu$ m
R <sub>mr01</sub> (50.0 %)	99.61 $\mu$ m
R <sub>mr01</sub> (50.0 %)	405.12 $\mu$ m

HOMMEL TESTER T1000

basic/top/wave



### **Appendix 12: *Calculations***

Calculation of the Number of Atomic Layers in a 0.0005 cm Layer of Gray Cast Iron

Assume a cubical piece of gray cast iron.

Density of Gray Cast Iron: 7.2 g/cm<sup>3</sup>

Atomic Weight of Iron = 55.85

Mass of iron in 1.0 cm x 1.0 cm x 0.0005 cm = 0.0005 cm<sup>3</sup> x 7.2 g/cm<sup>3</sup> = 0.0036 g

Number of Iron Atoms in 0.00367 g = (0.00367 g / 55.85) x 6.023 X 10<sup>23</sup> = 3.96 x 10<sup>19</sup>

Therefore each atom of iron occupies a volume = 0.0005 cm<sup>3</sup> / 3.96 x 10<sup>19</sup> = 1.26 x 10<sup>-23</sup> cm<sup>3</sup>

Assuming the volume occupied by each iron atom is cubical, then the length of the cube is the cube root of 1.26 x 10<sup>-23</sup> = 2.3 x 10<sup>-8</sup> cm

Therefore, the number of atomic layers in the stock needed to be removed to remove all of the grind lines  $\approx 0.0005 / 2.3 \times 10^{-8} \approx 22,000$  layers

At a stock removal rate of 1.0 layer per 0.30 second, it will take 22,000 layers / 1.0 layer/ 0.3 seconds  **$\approx 1.8$  hours**

**Appendix 13: Metallurgy, Second Edition, B. J. Moniz, American Technical Publishers, Inc., Homewood, IL 60430, 1994**

**Aluminum 325**

aluminum alloys. Heat-treatable aluminum alloys contain elements that are more soluble at elevated temperatures than at room temperature. When the solid solution is rapidly quenched, a supersaturated condition occurs. As the alloying elements precipitate out of the solution with the passage of time, the strength of the alloy increases. Artificial aging (precipitation hardening performed at elevated temperatures) is used to develop immediate maximum strength.

**Annealing.** Annealing is performed on heat-treatable and non-heat-treatable alloys to remove the effects of cold work. It is accomplished by heating within 300°C to 450°C (570°F to 840°F). The rate of softening depends on the time at temperature and can vary from several hours at low temperature to seconds at high temperature.

### Aluminum Designation Systems

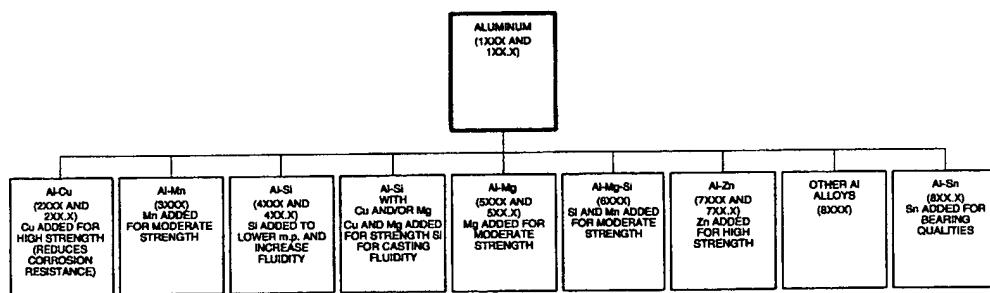
Aluminum and aluminum alloy products are identified by various designation systems, standards, and specifications. Aluminum products are covered by standards produced by the American Society for Testing and Materials, the Society of Automotive Engineers, and the Aerospace Materials Specifications.

Wrought and cast aluminum alloys are identified by various designation systems, which include the Aluminum Association (AA) numbering system and the Unified Numbering System for metals and alloys. See Figure 20-2. Aluminum Association designations for wrought aluminum alloys consists of four digits. The first digit indicates the major alloy-

ing element. For example, 2014 is an aluminum-copper alloy and 3003 is an aluminum-manganese alloy, both with specified chemical composition ranges. Aluminum Association designations for cast alloys consist of three numbers, a period, and a fourth number. The first number indicates the major alloying element. For most aluminum alloys, the fourth digit indicates the product form. Zero indicates the product form is a casting, a 1 for a standard ingot, and a 2 for an ingot with a narrower chemical composition range than a standard ingot. For example, 356.0 is an aluminum-silicon-copper-magnesium alloy casting with a specific chemical composition range, while 356.1 and 356.2 are similar alloys, but in ingot form and with slightly different chemical composition ranges.

**Temper designations** are letters that indicate the final condition of cold-worked (H) or heat-treated (T) material. The temper designation is separated from the alloy designation by a hyphen. For example, 3003-H2 designates a quarter hard aluminum-manganese alloy, and 2014-T4 designates an aluminum-copper alloy that is solution treated, quenched, and allowed to age at room temperature. See Figure 20-3.

The Unified Numbering System for metals and alloys identifies wrought and cast aluminum alloys with the uppercase letter A followed by five numbers that identify a composition range for a specific alloy. For wrought aluminum alloys, the first number is 9 followed by the Aluminum Association number for the alloy. For example, alloy 3003 is equivalent to UNS A93003. For cast aluminum alloys, the first number varies from 0 to 6. For example, alloy 356.0 is equivalent to UNS A03560.



**Figure 20-2.** Wrought aluminum alloys are designated by various systems, which include the Aluminum Association numbering system.

326 METALLURGY

TEMPER DESIGNATIONS	
Designation	Condition
F	As-fabricated
O	Annealed
H1	Strain hardened only
H2	Strain hardened and partially annealed
H3	Strain hardened and thermally stabilized
W	Solution heat treated
T1	Cooled from an elevated-temperature shaping process and naturally aged
T2	Cooled from an elevated-temperature shaping process, cold worked, and naturally aged
T3	Solution heat treated, cold worked, and naturally aged
T4	Solution heat treated and naturally aged
T5	Cooled from an elevated-temperature shaping process and then artificially aged
T6	Solution heat treated and then artificially aged
T7	Solution heat treated and stabilized
T8	Solution heat treated, cold worked, and then artificially aged
T9	Solution heat treated, artificially aged, and then cold worked
T10	Cooled from an elevated-temperature shaping process, cold worked, and then artificially aged

Figure 20-3. Temper designations are used to indicate the cold-worked or heat-treated condition of aluminum alloys.

**Wrought Aluminum Alloys.** The Aluminum Association designations for the wrought aluminum alloy series is 1xxx for commercially pure aluminum, 2xxx for aluminum-copper, 3xxx for aluminum-manganese, 4xxx for aluminum-silicon, 5xxx for aluminum-magnesium, 6xxx for aluminum-magnesium-silicon, 7xxx for aluminum-zinc, and 8xxx for aluminum-other elements. Chemical compositions and mechanical properties vary for the different wrought aluminum alloys.

The 1xxx series comprises commercially pure aluminum alloys containing >99.00% Al. The 1xxx series alloys have excellent corrosion resistance, high thermal and electrical conductivities, and excellent workability. These weak alloys are moderately strengthened by cold working and are used for chemical equipment, reflectors, heat exchangers,

electrical conductors and capacitors, packaging foil, architectural products, and decorative trim.

The 2xxx series comprises aluminum-copper alloys. The 2xxx series alloys are solution treated to achieve optimum mechanical properties. In some instances, these alloys are precipitation hardened, but this leads to a significant loss of elongation. The 2xxx series alloys are less corrosion resistant than most other aluminum alloys. To improve corrosion resistance, 2xxx series alloys are clad with high-purity aluminum or with an aluminum-magnesium-silicon alloy of the 6xxx series. The resulting alloy combination is an *alclad* product. An *alclad* is a composite wrought product comprised of an aluminum alloy core having, on one or both surfaces, a metallurgically bonded aluminum or aluminum alloy coating, which is resistant to corrosion. The 2xxx series alloys have high strength-to-weight ratios and are used for truck and aircraft wheels, truck suspension parts, aircraft fuselage, and wing skins. The weldability of the 2xxx series alloys is limited.

The 3xxx series comprises aluminum-manganese alloys. The 3xxx series alloys are strengthened by cold working and have approximately 20% more strength than the 1xxx series. See Figure 20-4. Alloys 3003, 3004, and 3105 are widely used for moderate strength applications requiring good workability. Applications include beverage cans, cooking utensils, heat exchangers, storage tanks, awnings, furniture, highway signs, roofing, siding, and other architectural forms.

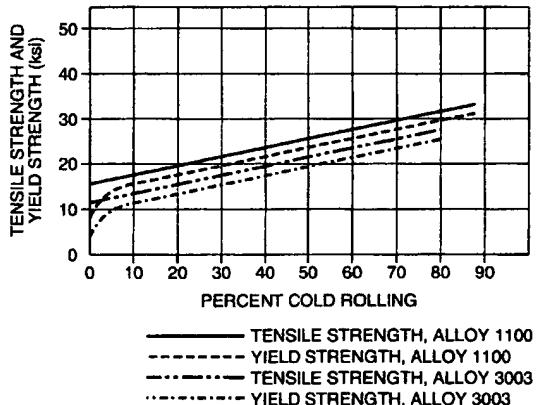


Figure 20-4. Aluminum-manganese (3xxx series) alloys may be heavily strain hardened during cold working.

The 4xxx series comprises aluminum-silicon alloys. Silicon may be added to aluminum in significant quantities (up to 12% Si), which causes lowering of the melting temperature range without embrittlement. See Figure 20-5. Consequently, 4xxx series alloys are often used for welding wire and as brazing filler metal. Although most 4xxx series alloys are not strengthened by heat treatment, when used for welding heat-treatable alloys, they will pick up some of the alloy content of the base metal and respond in a limited way to heat treatment. High-silicon alloys become dark gray to charcoal gray when anodized (specially treated to thicken the surface film) and are used in architectural applications. Alloy 4032, with 12.5% Si, has high wear resistance and is used for forged engine pistons.

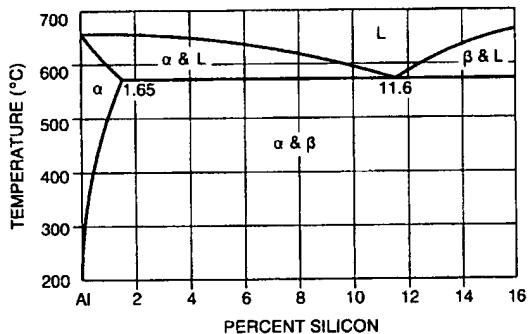
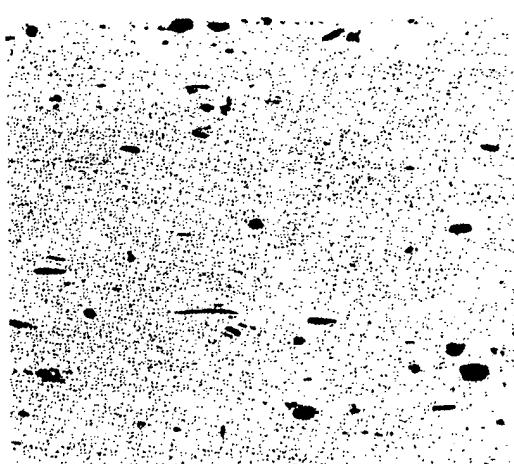
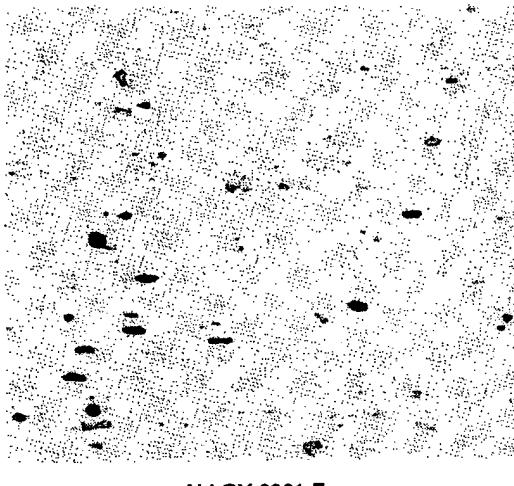


Figure 20-5. Silicon may be added to aluminum in significant quantities up to 12% Si.

The 5xxx series comprises aluminum-magnesium alloys, which are sometimes additionally alloyed with a small amount of manganese. Both elements cause solid solution hardening, although manganese is considerably more effective. The 5xxx series alloys have moderate to high strength, good weldability, and good marine corrosion resistance. To prevent stress-corrosion cracking, the amount of cold working must be limited in alloys with greater than approximately 3.5% Mg and in alloys that operate above 65°C (150°F). The 5xxx series alloys are used for architectural trim, decorative trim, cans and can ends, household appliances, bases for streetlights, boats and ships, cryogenic applications, and crane parts.

The 6xxx series comprises aluminum-silicon-magnesium alloys. The proportions of these ele-

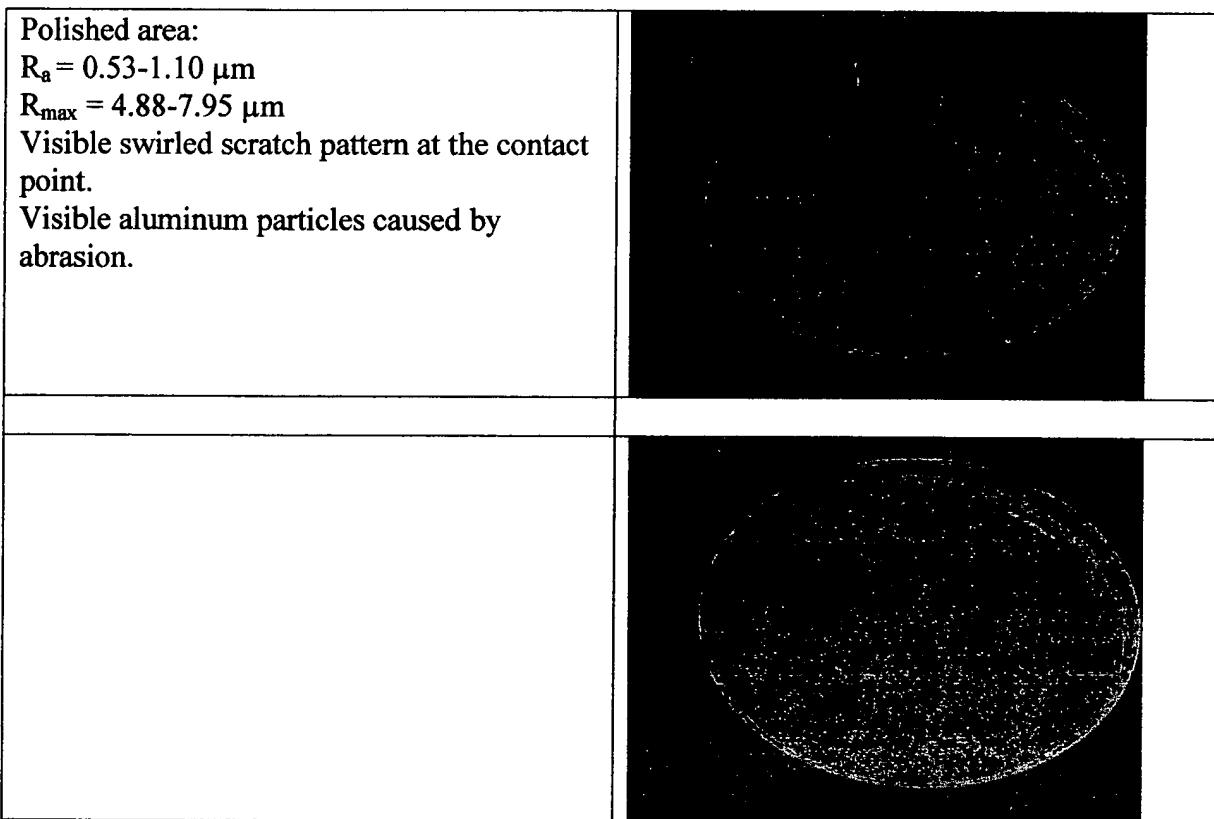
ments are adjusted to form the intermetallic compound magnesium silicide ( $Mg_2Si$ ). See Figure 20-6. The 6xxx series alloys are strengthened by precipitation hardening. These alloys have medium strength (less than the 2xxx or 7xxx alloys), formability, weldability, machinability, and corrosion resistance. The 6xxx series may be formed in the T4 (solution heat-treated) temper, and then precipitation hardened to the T6 temper. The 6xxx series alloys are



American Society for Metals

Figure 20-6. Alloy 6061-T6 is strengthened by magnesium silicide precipitation.

**Appendix 14:** Photographs of the aluminum specimen showing abraded particles after light rubbing and wetted with the alkaline dichromate solution for eight minutes.



**Appendix 15:** Photograph of the aluminum specimen showing abraded particles after light rubbing and wetted with only water for eight minutes.

